Pergamon

Cement and Concrete Research 30 (2000) 1801–1806

CEMENT AND CONCRETE RESEARCH

Prediction of hydroxyl concentrations in cement pore water using a numerical cement hydration model

R.J. van Eijk*, H.J.H. Brouwers

Department of Civil Engineering and Management, University of Twente, WB Building, P.O. Box 217, 7500 AE Enschede, Netherlands

Received 3 January 2000; accepted 23 August 2000

Abstract

In this paper, a 3D numerical cement hydration model is used for predicting alkali and hydroxyl concentrations in cement pore water. First, this numerical model is calibrated for Dutch cement employing both chemical shrinkage and calorimetric experiments. Secondly, the strength development of some standard mortars as predicted by the model is found to be in good agreement with performed experiments. Subsequently, alkali release and sorption, as well as the $Ca(OH)_2$ equilibrium are incorporated in the model. Finally, this extended hydration model is used to predict the pH development in cement pore water, which is found to correspond well with experiments reported in the literature. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Modelling; Hydration; Pore solution; Alkalis; pH

1. Introduction

In a hydrating cement paste concentrations of the pore water change continuously [1]. Knowing the concentration of ions is important for many reasons. For instance, the hydroxyl concentration and related pH are important parameters that determine the reactivity of cement additives. Fraay et al. [2] mentioned a threshold pH that was required for the reaction of fly ash. Song and Jennings [3] studied the effect of pH on the alkali activation of slags.

Cement is used as a binder in solidificaton/stabilization (S/S) processes for treating wastes. These wastes often contain metals (Zn, Cd) or borates that will precipitate as insoluble salts such as $Cd(OH)_2$ [4], $CaZn_2(OH)_6{\cdot}2H_2O$ [5], and $Ca[B(OH)_4]_2{\cdot}2H_2O$ [6]. These compounds may form an impermeable layer around the cement grains and thus inhibit further hydration reactions. Solubility and precipitation of these types of compounds obviously depend on both calcium and hydroxyl concentrations, which is the second motivation for determining the pH of the pore water. In order to describe the effects of the presence of these ions during cement hydration, the relevant chemical equilibria should be taken into account.

In this paper, CEMHYD3D is used, a numerical cement hydration model that was developed at NIST and is described in detail by Bentz [7]. The model simulates the reactions between cement clinker minerals and water. It starts with a digital matrix of pixels with a unit size of 1 μm^3, which are assigned to water, gypsum or one of the cement mineral phases. A simulation consist of dissolution cycles in which solid phases are scanned and can dissolve, react, diffuse and precipitate as $Ca(OH)_2$ (CH) or calcium-silicate hydrate (C-S-H). After each hydration cycle, it predicts the hydration degree, the porosity and the phase composition of the present microstructure. The model has been very successful in predicting temperature rises [8] and for investigating relations between particle size distribution, w/c ratio and hydration degree [9]. The model has been calibrated for American [7] and French [8] cements. Here, the model is calibrated for Dutch cements.

The first step for using the CEMHYD3D model to calculate pore water concentrations is the implementation of Taylor's empirical theory [10], which describes the release of alkalis from cement and alkali sorption by the hydration products formed. This theory includes a number of steps and empirical equations and parameters required to calculate pore water concentrations. In this paper, using

---

* Corresponding author. Tel.: +31-53-489-4883; fax: +31-53-489-2511.

E-mail address: r.j.vaneijk@sms.utwente.nl (R.J. van Eijk).

0008-8846/00/$ – see front matter
PII: S0008-8846(00)00413-0

Taylor's model and a simplified set of equilibria, the CEMHYD3D model is extended. With this extended model, both the microstructure development and pore water hydroxyl concentrations can be calculated straightforwardly. The pH predictions by the hydration model are compared with measurements reported in the literature.

2. Calibration and strength development

The cement hydration model has been validated successfully for American Portland cements [7] and the French Montalieu cement [8]. Here it will be validated for two Dutch cements which possess the same oxide composition, but have different particle size distributions: type CEM I 32,5 R and CEM I 52,5 R (Blaine surfaces of 286 and 489 m^2/kg, respectively). The oxide composition of Dutch ordinary Portland cement (OPC) is given in Table 1. The physical density of the cements was 3150 kg/m^3. Calibration of the model results in a parameter B that relates calculation cycles with true time according to a quadratic relation given by Bentz [7] and based on parabolic hydration kinetics:

$$t\ (\text{hours}) = t_0 + B(\text{cycles})^2 \tag{1}$$

where t = hydration time; t_0 = induction period; cycles = number of executed calculation cycles; B = calibration parameter.

Two different techniques were used to measure hydration degree as a function of time: calorimetry and chemical shrinkage. The mass fractions of the main clinker minerals in the cement were calculated from the oxide composition using the modified Bogue method [1]. From the hydration enthalpy for each mineral phase [1] and the mineral composition, a heat release of 54 kJ per 100 g of fully hydrated OPC paste was found. Chemical shrinkage is defined as the volume reduction of a hydrating cement paste as a result of volume differences between starting materials and hydration products. In a water-saturated system, this volume reduction is compensated by absorbing extra water from the environment. This absorbed water volume can be measured. From the volume stoichiometries of all relevant hydration reactions, the chemical shrinkage for a fully hydrated paste was calculated as 6.9 ml per 100 g hydrated OPC.

Table 1
Cement compositions

	Cement used for calibration	Cement used for pore water calculation [23]
CaO	64.40	61.90
SiO_2	20.36	19.94
Al_2O_3	4.96	5.57
Fe_2O_3	3.17	2.91
K_2O	0.64	0.82
Na_2O	0.14	0.21
SO_3	2.57	3.10
MgO	2.09	1.50
TiO_2	0.35	–
Mn_3O_4	0.14	–
P_2O_5	0.18	–
LOI	0.88	0.55

Table 2
Measured hydration degrees

	CEM I 32,5 R		CEM I 52,5 R	
Days	Chemical shrinkage	Calorimetry	Chemical shrinkage	Calorimetry
1	0.25	0.26	0.44	0.42
2	0.33	0.37	0.54	0.54
3	0.38	0.44	0.58	0.58
7	0.41	0.54	0.69	0.64

Calorimetric measurements were performed on cement pastes having a w/c ratio of 0.4. Heat of hydration was measured under isotherm conditions at a temperature of 20°C during 7 days. Chemical shrinkage was measured following the method of Tazawa et al. [11]. Cement pastes (w/c = 0.4) were placed in a glass jar and 1 ml of extra water was placed on the paste surface. The jar was filled up with hydraulic oil and sealed with a rubber stop in which a pipette was placed. One control sample was prepared that only contained cement and oil in order to correct for temperature differences. All samples were placed in a 20°C water tub during the whole experiment. The volume of water taken up by the hydrating cement paste was measured by reading the oil level. Values were corrected using the control sample and calculated per gram of OPC present in each sample. Table 2 shows the hydration degrees determined by both calorimetry and chemical shrinkage. Both methods appeared to produce similar results.

This information was used for determining the parameters in Eq. (1). The chemical composition and particle size distributions of the cements were used to reconstruct a 3D representation of the cement at a w/c of 0.4. This system included 5% (m/m) of gypsum consisting of particles of size 1–11 μm. Simulations were conducted at a constant temperature of 20°C under saturated conditions. Best results were obtained for t_0 = 6.7 h and B = 0.0010. These values hold for both Dutch CEM I 32,5 R and CEM I 52,5 R, which differ in particle size distribution, only. Values of t_0 = 6.7 h and B = 0.0017 [7] and t_0 = 7.5 h and B = 0.0011 [8] were reported for American and French cements, respectively.

The strength of mortar cubes is related to the gel–space ratio as defined by Powers [12] and calculated as follows [Eq. (2)]:

$$X = \frac{0.68\alpha}{0.32\alpha + \text{w/c}} \tag{2}$$

where X = gel/space ratio; α = hydration degree; w/c = water/cement ratio.Compressive strength is related to this gel–space ratio according to the relation:

$$F_c = F_0 X^n \tag{3}$$

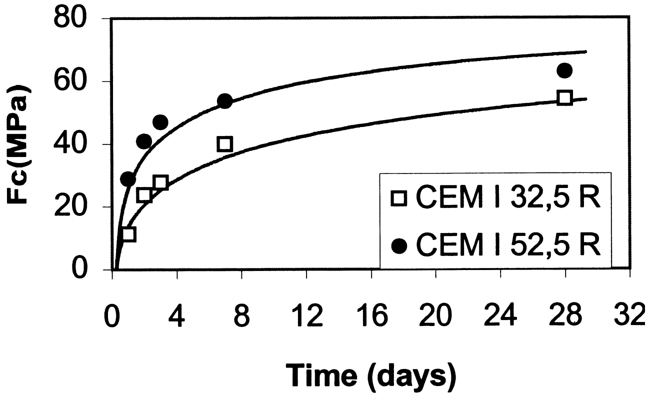

Fig. 1. Calculated and measured strength.

where F_c is compressive strength [N/mm^2], and F_0 represents the intrinsic strength of the cement gel. Using the calibrated hydration model, the developments of hydration degree were determined. Using Eq. (3), the corresponding compressive strengths were calculated with parameters $n=2.2$ and $F_0=135$ N/mm^2 for both cements. Fig. 1 shows the calculated strength development compared to measured strengths. The strength was measured according to the standard NEN-EN 196-1 [13]. From Fig. 1, it follows that strength development is predicted well by the model.

3. Pore water concentrations

The pore solution is assumed to be saturated in $Ca(OH)_2$ during cement hydration. During cement hydration, substantial amounts of alkalis (sodium and potassium) are released. This is a result of the dissolution of alkali sulfates and the reaction of cement clinker phases. While the ion products of both KOH and NaOH and the corresponding sulfates are significantly higher compared to that of $Ca(OH)_2$, it is assumed that the solution is always saturated with regard to $Ca(OH)_2$. According to Taylor [10], most sulfates enter products of low solubility and are exchanged for [OH^-]. Therefore, it was assumed that the amount of [OH^-] released from cement is equal to the amount of alkali released. In this study, the CH equilibrium will be taken into account, because it is of importance for describing precipitation reactions that occur in the first minutes after mixing cement and water and waste [4–6].

According to Taylor [10], all water present in reaction products should not be considered as the pore water in which all ions are dissolved. Therefore, in the pore water modelling studies by Reardon [14], water mass balance expressions were used to distribute the total mass of water between hydration products and pore water available for the dissolution of ions. CEMHYD3D is based on a number of hydration products with fixed stoichiometries and fixed water contents. Thus, during a simulation, the amount of unreacted water can be directly determined from the amount of water that is part of one of the formed hydration products. Furthermore, vacuum (self-desiccation) and air voids do not occur (assuming hydration under water-saturated conditions), so all porosity is completely filled with water. Hence, the porosity volume fraction calculated by CEMHYD3D equals the pore water fraction containing available for the dissolution of ions. Taking this into account, it is possible to calculate [OH^-] and [Ca^{2+}] concentrations as a function of hydration degree and time from the total number of moles of alkali released (sum of Na^+ and K^+) into the pore water, and the known ion product for $Ca(OH)_2$.

Taylor [10] developed a method to describe the alkali content in cement pore water. It is based on the total alkali content in cement, the w/c ratio used and the hydration degree. When the release and uptake of alkalis in reaction products and the porosity fraction is known, the concentration of alkalis and corresponding [OH^-] can be predicted during hydration.

The total numbers of moles of Na^+ and K^+ present per gram of cement were calculated from the corresponding mass fractions and molecular masses. For Na, the calculation is as follows [Eq. (4)]:

$$\mathrm{Na_T} = \frac{f_{\mathrm{Na_2O}} \cdot 2}{\mathrm{MM_{Na_2O}}} \tag{4}$$

where $\mathrm{Na_T}$ = total Na content [mol/g]; $f_{\mathrm{Na_2}}\mathrm{O}$ = Na_2O mass fraction [g/g]; $\mathrm{MM_{Na_2}O}$ = molar mass of Na_2O [g/mol].

Alkalis in cement are partly present as readily soluble sulfates at the surface of cement grains and partly bound in the clinker minerals [1]. The fraction of alkalis present as sulfate will be present in solution before any hydration takes place. The remaining fractions of alkalis are released during hydration. Pollit and Brown [15] studied the distribution of alkalis and SO_3 in many clinkers with different amounts of alkalis and sulfates. From their data, it was assumed that in the Dutch cements 35% and 70% of Na and K, respectively, are present as readily soluble sulfates. The amount of Na^+ released immediately is calculated as follows:

$$[Na^+]_{sulfate} = \frac{f_{Na,sulfate} Na_T m_c}{\frac{\phi_{por}}{\phi^0_{por}} \frac{m_w}{\rho_w}} = \frac{f_{Na,sulfate} Na_T}{\frac{\phi_{por}}{\phi^0_{por}} w/c} \rho_w \tag{5}$$

where $[Na^+]_{sulfate} = Na^+$ released from sulfates [mol/l]; $f_{Na,sulfate}$ = fraction of Na present as sulfate; m_c = mass cement [g]; m_w = mass water [g]; $(\phi_{por}/\phi_{por}{}^0)$ = concentration concentration factor; ρ_w = water density = 1000 [g/dm^3]; w/c = water/cement ratio.It is assumed that the alkalis bound in the clinker mineral will be released into the pore water as soon as the clinker reacts and dissolves. The amount of Na^+ released from the clinker is thus linear proportional with the hydration degree:

$$[Na^+]_{clinker} = \frac{(1 - f_{Na,sulfate}) Na_T \alpha m_c}{\frac{\phi_{por}}{\phi^0_{por}} \frac{m_w}{\rho_w}} = \frac{(1 - f_{Na,sulfate}) Na_T \alpha}{\frac{\phi_{por}}{\phi^0_{por}} w/c} \rho_w \tag{6}$$

where $[Na^+]_{clinker} = Na^+$ released from clinker [mol/l]; α = hydration degree.

The concentration factor used in Eqs. (5) and (6) is defined as the ratio of the porosity fraction to the initial porosity fraction. It is assumed that all porosity is completely filled with pore water and equals the amount of free water present in the system that also contains all ions of interest. The concentration factor is introduced to account for the decrease in porosity (water) during hydration and is therefore α dependent. As a result of this decrease in porosity, all ions present in the pore solution are concentrated correspondingly. The total number of moles of Na released per liter of pore water and before any uptake by sorption is the sum of Na released from sulfates and from clinker minerals. This sum is [Eq. (7)]:

$$[Na^+]_{released} = [Na^+]_{sulfate} + [Na^+]_{clinker} \tag{7}$$

Taylor [1] discusses the amount of each alkali cation taken up by the hydration products, C-S-H and AFm; it is proportional to the concentration present in the solution and the quantity of these hydration products formed. All alkalis are both released and consumed with equivalent amounts of OH^- ions. Taylor [10] introduced two empirical constants, called binding factors, which are numerically equal to the amount of alkali in millimoles that can be taken up from a 1 M alkali solution by the total quantity of hydration products formed from 100 g OPC. From his data, Taylor [10] assumed binding factors of 0.31 and 0.20 mmol alkali sorbed per gram of hydrated OPC and per mole per liter of total alkali released into the pore water for Na^+ and K^+, respectively. The proportional relation between amount of alkali present in solution and amount sorbed by hydration product has been confirmed by Hong and Glasser [16] who used synthetic C-S-H. They found no significant difference in the binding capacities for Na^+ and K^+. In this study, binding factors of 0.30 and 0.27 were assumed for Na^+ and K^+, respectively. Hence, the amount of Na^+ consumed in mole per liter is [Eq. (8)]:

$$[Na^+]_{consumed} = \frac{b_{Na} \alpha m_c [Na^+]_{released}}{m_w} = \frac{b_{Na}\alpha}{w/c}[Na^+]_{released} = \frac{b_{Na} Na_T \rho_w \alpha^2}{\frac{\varphi_{por}}{\varphi^0_{por}} (w/c)^2} \tag{8}$$

where b_{Na} = alkali binding factor = 0.30 ml/g.

Calculations for $[K^+]$ are done using the same equations and the corresponding values for K^+. The difference between the amounts of alkali released and consumed gives the actual alkali concentration in cement pore water [Eq. (9)].

$$[Na^+ + K^+] = [Na^+]_{released} - [Na^+]_{consumed} + [K^+]_{released} - [K^+]_{consumed} \tag{9}$$

Immediately after mixing cement and water the pore solution is saturated with respect to CH. The corresponding solubility product, $k_{CH}{}^0$, was taken from the database used in SOLTEQ [17,18], the chemical equilibrium model developed by Batchelor and based on MINTEQA2 [19]. This thermodynamic value was used in all calculations. All concentrations used in the equations and in our calculations are in molar units [Eq. (10)].

$$k^0_{CH} = [Ca^{2+}][OH^-]^2 \gamma_{Ca} \gamma^2_{OH} = 10^{-5.19} = 6.46 \cdot 10^{-6}\ [mol^3/dm^9] \tag{10}$$

where γ = activity coefficient.

The corresponding activity coefficients were estimated using the Davies equation for single ions [20]. The corresponding concentration product, k_{CH}, is then related to the thermodynamic solubility product $k_{CH}{}^0$ as follows:

$$k_{CH} = \frac{k^0_{CH}}{\gamma_{Ca}\gamma^2_{OH}} = [Ca^{2+}][OH^-]^2 \tag{11}$$

If excess of a solid phase is in equilibrium with the solution, the total amount of that compound in solution is called the molar solubility, denoted by S [20]. In a solution that contains $Ca(OH)_2$, the molar solubility is denoted S_{CH}.

In a saturated solution of an ionic salt, addition of another, more soluble salt containing one of those ions, will decrease the solubility of the first. This is known as the "common-ion effect." The $[OH^-]$ ions in solution originates both from the dissolution of $Ca(OH)_2$ and from the total amount of alkali $[Na^+ + K^+]$ released into the pore water. As long as solid CH is present the following relations hold:

$$[Ca^{2+}] = S_{CH} \tag{12}$$

$$[OH^-] = 2S_{CH} + [Na^+ + K^+] \tag{13}$$

Table 3
Calculated and measured pore water concentrations

Time (days)	Hydration degree (α)	(ϕ_{por}/ϕ^0_{por})	[$Na^+ + K^+$]	$10^{-3}\cdot[Ca^{2+}]$	[OH^-] calculated	[OH^-] measured
0.25	0	1.00	0.32	1.54	0.33	0.12
0.50	0.22	0.82	0.39	1.05	0.40	0.13
1	0.31	0.75	0.42	0.91	0.42	0.14
2	0.39	0.70	0.44	0.82	0.44	0.21
3	0.44	0.67	0.46	0.78	0.46	0.27
7	0.54	0.61	0.48	0.69	0.48	0.41
14	0.62	0.56	0.50	0.64	0.50	0.45
28	0.7	0.52	0.52	0.59	0.52	0.47

Furthermore, the water ionisation constant relates [OH^-] and [H^+] as follows [Eq. (14)]:

$$k_w = [H^+][OH^-] = 10^{-14} \tag{14}$$

Substituting Eqs. (12) and (13) into the concentration product [Eq. (11)] yields the following equation [Eq. (15)]:

$$\begin{aligned} k_{CH} = [Ca^{2+}](2[Ca^{2+}] + [Na^+ + K^+])^2 = 4[Ca^{2+}]^3 \\ +4[Na^+ + K^+][Ca^{2+}]^2 + [Na^+ + K^+]^2[Ca^{2+}] \end{aligned} \tag{15}$$

For a known alkali concentration, this equation is dependent in [Ca^{2+}] only and can be solved in closed form using the computer program MATHEMATICA [21]:

$$[Ca^{2+}] = \frac{([Na^+ + K^+] - X)^2}{6X},$$

$$X = \sqrt[3]{([Na^+ + K^+]^3 + 27\cdot k_{CH} + 3\sqrt{3}\cdot\sqrt{k_{CH}}\cdot\sqrt{2\cdot[Na^+ + K^+]^3 + 27\cdot k_{CH}})} \tag{16}$$

When [Ca^{2+}] is calculated, [OH^-] can be calculated from the concentration product [Eq. (11)] and subsequently, the pH can be determined from the relation $pH = 14 + \log[OH^-]$.

Table 3 contains the hydration degrees and concentration factors (porosity/initial porosity ratios) obtained by the calibrated cement hydration model for a CEM 32,5 R cement and the calculated pore water concentrations. As expected, the alkali concentration increases and this results in a decrease in [Ca^{2+}] and a corresponding increase in [OH^-] according to the CH equilibrium [see Eq. (11)]. In general, [OH^-] equals [$Na^+ + K^+$] and the pore water can be considered as an alkali hydroxide solution saturated with respect to $Ca(OH)_2$. Because alkali concentrations are significantly present as from the beginning of hydration, CH equilibrium is more relevant for calculating [Ca^{2+}] than for calculating [OH^-]. Calcium concentrations are very low from the start of hydration, which is in agreement with experiments [22].

Additional calculations with lower alkali contents in the cement showed that CH equilibrium will only effect [OH^-] when [$Na^+ + K^+$] < 0.2 M, which may be the case during the first day of hydration when alkali content is low (Na_2O equivalent $< 0.6\%$) or when the total fraction of alkali present as readily soluble sulfates is lower than 0.5. The CH equilibrium is also relevant when [$Na^+ + K^+$] $= 0$, as will be the case for hydration of pure C_3S and/or C_2S. Substituting [$Na^+ + K^+$] $= 0$ into Eq. (16) indeed yields [Eq. (17)]:

$$[Ca^{2+}] = \sqrt[3]{\frac{k_{CH}}{4}} \tag{17}$$

which is simply the solution of Eqs. (11) and (12) for an alkali-free saturated $Ca(OH)_2$ solution. Taking $\gamma_{Ca} = 0.43$ and $\gamma_{OH} = 0.80$, this yields [Ca^{2+}] $= 0.018$ M and [OH^-] $= 0.036$ M.

Table 3 and Fig. 2 also show the results from Larbi et al. [23] who determined pore water concentrations in pastes prepared with Dutch OPC at a w/c ratio of 0.45. Pore water was obtained using a pore fluid expression apparatus similar to that used by Longuet et al. [22]. Curing took place at a temperature of 20°C and [OH^-] in the pore water was determined by titration against HNO_3 and phenolphthalein as an indicator. As can be seen from Fig. 2, there is a good agreement between calculated and measured hydroxyl concentrations after 7 days of hydration. The disagreement in earlier period of hydration can be explained by the presence of sulfates. Especially during the first day, when there is still solid gypsum present in the system, sulfate concentrations will be significant and because of charge balance this will result in [OH^-] being lower than [$Na^+ + K^+$]. This was not accounted for in the present calculations.

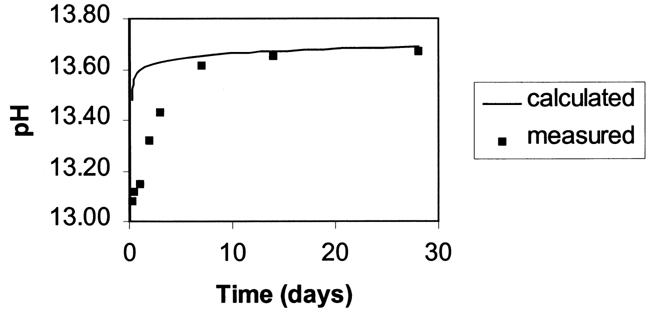

Fig. 2. Pore water pH development.

4. Conclusions

A cement hydration model (CEMHYD3D) was calibrated for Dutch cements (CEM I 32,5 R and CEM I 52,5 R) using both chemical shrinkage and calorimetric measurements. Both methods yield similar hydration degrees (Table 2) and yield as values: $t_0 = 6.7$ h and $B = 0.0010$ for CEMHYD3D. Furthermore, the calibrated model was able to predict strength development quite well (Fig. 1).

Next, the calibrated model was used to describe hydration degree, alkali release and decrease in amount of pore water as a function of time. From these parameters and the alkali content of the cement and Taylor's alkali sorption model, the concentrations of alkalis and calcium and the pH development were calculated. The observed trends agreed well with experimental results reported in the literature. The pH as from 7 days of hydration could be reasonably predicted using the equations derived. The calculations showed that at that time, pH is mostly determined by alkali concentrations. The present results are useful for specifying the general mixture conditions and pertaining the time required to reach the threshold pH for activating fly ash and slag reactions.

In order to predict the pH in the early hydration period, especially during the first day, the gypsum equilibrium should be taken into account. For more accurate results, in general, also the sulfate phase equilibria, e.g. ettringite and AFm, should be accounted for. This will be the subject of further work.

Acknowledgments

The authors wish to express their gratitude to Dr. ir. J. Blaakmeer and Mr. M. de Loo of ENCI for their cooperation, supply of binders, execution of analyses, strength measurements and calorimetry. Furthermore, they would like to thank Mr. H.M. Menkehorst from the University of Twente for his help in performing the chemical shrinkage measurements.

References

[1] H.F.W. Taylor, Cement Chemistry, 2nd edn., Thomas Telford, London, 1997.

[2] A.L.A. Fraay, J.P. Bijen, Y.M. de Haan, The reaction of fly ash in concrete. A critical examination, Cem Concr Res 19 (1989) 235–246.

[3] S. Song, H.M. Jennings, Pore solution chemistry of alkali-activated ground granulated blast-furnace slag, Cem Concr Res 29 (1999) 159–170.

[4] J.M. Diez, J. Madrid, A. Macias, Characterization of cement-stabilized Cd wastes, Cem Concr Res 27 (3) (1997) 337–343.

[5] M. Yousouf, A. Mollah, R.K. Vempati, T.-C. Lin, D.L. Cocke, The interfacial chemistry of solidification/stabilization of metals in cement and pozzolanic material systems, Waste Manage 14 (2) (1995) 137–148.

[6] J.M. Casabonne Masonnave, Immobilization of borates and phosphate anion with saturated lime solutions, Solid State Ionics 59 (1993) 133–139.

[7] D.P. Bentz, Three-dimensional computer simulation of portland cement hydration and microstructure development, J Am Ceram Soc 80 (1) (1997) 3–21.

[8] D.P. Bentz, V. Waller, F. de Larrard, Prediction of adiabatic temperature rise in conventional and high-performance concrete using a 3-D microstructural model, Cem Concr Res 28 (2) (1998) 285–297.

[9] D.P. Bentz, C.J. Haecker, An argument for using coarse cements in high-performance concretes, Cem Concr Res 29 (1999) 615–618.

[10] H.F.W. Taylor, A method for predicting alkali ion concentrations in cement pore solutions, Adv Cem Res 1 (1987) 5–16.

[11] E. Tazawa, S. Miyazawa, T. Kasai, Chemical shrinkage and autogeneous shrinkage of hydrating cement paste, Cem Concr Res 25 (2) (1995) 288–292.

[12] T.C. Powers, in: 4th ISCC, US Department of Commerce, Washington, D.C., Vol. 2, (1962) 577.

[13] NEN-EN 196-1, Nederlands Normalisatie Instituut, Delft (in Dutch), 1995.

[14] E.J. Reardon, Problems and approaches to the prediction of the chemical composition in cement/water systems, Waste Manage 12 (1992) 221–239.

[15] H.W.W. Pollit, A.W. Brown, in: 5th ISCC, Cement Association of Japan, Tokyo, Vol. 1, (1969) 322.

[16] S.-Y. Hong, F.P. Glasser, Alkali binding in cement pastes: Part I. The C-S-H phase, Cem Concr Res 29 (2000) 1893–1903.

[17] B. Batchelor, K. Wu, Effects of equilibrium chemistry on leaching of contaminants from stabilized/solidified wastes, in: R.D. Spence (Ed.), Chemistry and Microstructure of Solidified Waste Forms, Lewis Publishers, Boca Raton, FL, 1993, pp. 243–258.

[18] J.-Y. Park, B. Batchelor, Prediction of chemical speciation in stabilized/solidified wastes using a general chemical equilibrium model: Part I. Chemical representation of cementitious binders, Cem Concr Res 29 (1999) 361–368.

[19] J.D. Allison, D.S. Brown, K.J. Novo-Gradac, Minteqa2/Prodefa2, A geochemical assessment model for environmental systems: Version 3.0 User's Manual, EPA/600/3-91/021, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, GA, 1991.

[20] J.N. Butler, Ionic equilibrium, Solubility and pH Calculations, Wiley, New York, 1998.

[21] S. Wolfram, MATHEMATICA, 2nd edn., Addison-Wesley Publishing, Redwood City, CA, 1991.

[22] P. Longuet, L. Burglen, A. Zelwer, The liquid phase of hydrated cement, Rev Mat Constr (France) 676 (1973) 35–41.

[23] J.A. Larbi, A.L.A. Fraay, J.M.J.M. Bijen, The chemistry of the pore fluid of silica fume-blended cement systems, Cem Concr Res 20 (4) (1990) 506–516.